Non-degenerate perturbation theory

The Hamiltonians we have diagonalized so far were all very simple and special. However, there are many situations of practical interest which involve more complicated Hamiltonians that cannot be diagonalized analytically.

What do we do in these cases? Do we give up? No! Never! Physicists never give up! We always find a way. In fact, there are 2 ways: one is to solve the problem numerically and the other is to use approximation methods.

Numerical solutions are the way to go in classical mechanics since solving Newton's Eq numerically is quite easy.

In QM, numerical methods are becoming more and more popular, but they will always have limitations, for 2 reasons. One, the size of the Hilbert space increases exponentially with the number of particles in the system. And 2, in QM it is the probability amplitudes which change with time, not the probabilities; ie, we can't roll dice in QM.

For this reason, approximation methods are very important. In fact, when you start dealing with many-body problems in condensed matter physics and with particle physics in quantum field theory, we realize that approximation methods are the key to success

Approximation methods always involve finding a small quantity, and then making some type of series expansion over it. In QM this is called perturbation theory.

This theory started with Schrödinger himself, just a few months after he first published his famous Eq. In his first paper he applied his Eq. to the H-atom and found the Bohr energy levels. He then went to study the hydrogen atom under the effect of an electric field, something called the Stark effect. But he soon found out that he couldn't diagonalize the problem exactly; it was just too complicated. So he developed perturbation theory, an approximation method which is good for small electric fields. His results agreed very well with experiment.

Whenever we expand something in a series, we must always ask if this series will converge. This is a big problem in quantum mechanics, as we will later discuss.

In quantum field theory, scientists have been able to improve substantially on this difficulty. They devised something called the renormalization group (fancy name!) in which you can know in advance, whether your series will converge or not.

Maybe you have heard about the difficulty of unifying gravitation (general relativity) with quantum field theory. The problem is precisely that the series of the gravitational force does not converge. We say gravity is not renormalizable.

References: Griffiths 6.1 Pauling 22 (only 1st order)
Sakurai 5.1 (confusing) Gottfried (cool but abstract)

Formal Framework

Suppose we are given a Hamiltonian $\hat{H}$ which we want to diagonalize:

$$\hat{H}|m\rangle = E_m|m\rangle \tag{1}$$

ut we can't do it; its too hard. However, suppose it turns out hat $\hat{H}$ can be written as

$$\hat{H} = \hat{H}_0 + \lambda\hat{V} \tag{2}$$

here λ is a small parameter and $\hat{H}_0$ is a Hamiltonian ve happen to know how to diagonalize

$$\hat{H}_0|m_0\rangle = E_m^0|m_0\rangle \tag{3}$$

Our strategy then is to try to find the eigenstuff of $\hat{H}$ pproximately, using the fact that λ is small. the key idea hat when $\lambda \to 0$ both E_m and $|m\rangle$ should tend continuously to E_m^0 and $|m_0\rangle$. Thus we can try to expand them n a power series in λ. the energy is therefore written s

$$E_m = E_m^0 + \lambda E_m^1 + \lambda^2 E_m^2 + \ldots \tag{4}$$

n many cases $E_m^1 = 0$ so we want to be able to find t least E_m^2.

We do something similar to the eigenvectors. Since the $m_0\rangle$ form an orthogonal basis we may expand

$$|m\rangle = \sum_m b_m|m_0\rangle$$

The coefficients b_n will depend on λ, so if we expand them in a power series we obtain

$$|m\rangle = |m_0\rangle + \lambda |m_1\rangle + \lambda^2 |m_2\rangle + \dots \qquad (5)$$

we may say something about these vectors by looking at the normalization of $|m\rangle$. By definition $\langle m_0|m_0\rangle = 1$, but we also want $\langle m|m\rangle = 1$. Thus

$$1 = \langle m|m\rangle = \langle m_0|m_0\rangle + \lambda\left[\langle m_0|m_1\rangle + \langle m_1|m_0\rangle\right] + \mathcal{O}(\lambda)^2 \quad ($$

Since $\langle m_0|m_0\rangle = 1$, all higher order terms must be zero. In particular

$$\langle m_0|m_1\rangle = 0 \qquad (7)$$

Ok! Now we write Eq (1) as $(\hat{H} - E_m)|m\rangle = 0$ and multiply on the left by $\langle n_0|$:

$$0 = \langle n_0|\hat{H} - E_m|m\rangle = \langle n_0|\hat{H}_0|m\rangle + \lambda\langle n_0|\hat{V}|m\rangle - E_m\langle n_0|m$$

But $\langle n_0|\hat{H}_0|m\rangle = E_n^0 \langle n_0|m\rangle$ so we obtain

$$\boxed{(E_m - E_n^0)\langle n_0|m\rangle = \lambda\langle n_0|\hat{V}|m\rangle} \qquad (8.$$

this Eq is exact. Now we insert Eq (5) but go only up to linear order in λ. We also assume that $n \neq m$. Then

$$\langle n_0|m\rangle = \langle n_0|m_0\rangle + \lambda\langle n_0|m_1\rangle + \mathcal{O}(\lambda)^2 = \lambda\langle n_0|m_1\rangle$$

since $\langle n_0|m_0\rangle = 0$ for $n \neq m$.

Similarly

$$\lambda\langle m_0|\hat{V}|n\rangle \approx \lambda\langle m_0|\hat{V}|n_0\rangle + \lambda^2\langle m_0|\hat{V}|n_1\rangle$$

But the second term is of order λ^2, so we may neglect it.
Hence Eq (8) becomes

$$(E_n - E_m^0)\langle m_0|n_1\rangle = \langle m_0|\hat{V}|n_0\rangle$$

Now we also need to expand E_n. But we may only keep E_n^0 since the term λE_n^1 will already be an order larger in λ.

Hence

$$\boxed{\langle m_0|n_1\rangle = \frac{\langle m_0|\hat{V}|n_0\rangle}{E_n^0 - E_m^0}} \qquad (9)$$

Notice that this will only work is the spectrum of $\hat{H}_0$ is non-degenerate. This is very important, otherwise we would divide by 0, which is a sin. Also, since $\langle n_0|n_1\rangle = 0$, we only need to worry about $m \neq n$.

Since the $|m_0\rangle$ form a basis we may write

$$|n_1\rangle = \sum_m |m_0\rangle\langle m_0|n_1\rangle$$

So, the eigenvectors to first order in λ are, from (5)

$$\boxed{|n\rangle = |n_0\rangle + \lambda\sum_{m\neq n}\frac{\langle m_0|\hat{V}|n_0\rangle}{E_n^0 - E_m^0}|m_0\rangle + \mathcal{O}(\lambda)^2} \qquad (10)$$

Now we find the eigenvalues. For this we use Eq (8), but now with $n = m$:

$$(E_m - E_m^0) \langle m_0 | m \rangle = \lambda \langle m_0 | \hat{V} | m \rangle$$

or

$$E_m - E_m^0 = \lambda \frac{\langle m_0 | \hat{V} | m \rangle}{\langle m_0 | m \rangle}$$

Using (5) we get

$$\langle m_0 | m \rangle = \langle m_0 | m_0 \rangle + \lambda \langle m_0 | m_1 \rangle + \lambda^2 \langle m_0 | m_2 \rangle + \cdots$$
$$\approx 1 + \lambda^2 \langle m_0 | m_2 \rangle$$

$$\lambda \langle m_0 | \hat{V} | m \rangle = \lambda \langle m_0 | \hat{V} | m_0 \rangle + \lambda^2 \langle m_0 | \hat{V} | m_1 \rangle + \mathcal{O} (\lambda)^3 .$$

If we stick to order up to λ^2 only then the term $\langle m_0 | m_2 \rangle$ in the denominator will not contribute. Thus, even though we have found the eigenvectors to first order in λ, the eigenvalue are correct up to order λ^2:

$$\boxed{E_m = E_m^0 + \lambda \langle m_0 | \hat{V} | m_0 \rangle + \lambda^2 \langle m_0 | \hat{V} | m_1 \rangle + \mathcal{O}(\lambda)^3} \qquad (11)$$

Using (10) we finally arrive at

$$\boxed{E_m = E_m^0 + \lambda \langle m_0 | \hat{V} | m_0 \rangle + \lambda^2 \sum_{n \neq m} \frac{|\langle n_0 | \hat{V} | m_0 \rangle|^2}{E_m^0 - E_n^0} + \mathcal{O}(\lambda)^3} \qquad (1$$

This is the result we wanted. It gives the corrected energies up to order λ^2 for the non-degenerate case.

Sanity checks using the harmonic oscillator

Consider the Harmonic oscillator

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2 = \hbar\omega(\hat{a}^\dagger \hat{a} + 1/2) \qquad (13)$$

here $\hat{x} = \frac{x_0}{\sqrt{2}}(\hat{a}^\dagger + \hat{a})$ and $\hat{p} = \frac{i p_0}{\sqrt{2}}(\hat{a}^\dagger - \hat{a})$, with $x_0 = \sqrt{\frac{\hbar}{m\omega}}$ nd $p_0 = \hbar/x_0$. The unperturbed energies are

$$E_n^0 = \hbar\omega(n + 1/2), \quad n = 0, 1, 2, \dots \qquad (14)$$

Particle in an electric field

Suppose this particle is also subject to an electric field ith potential

$$\hat{V} = -q\mathcal{E}\hat{x} \qquad (15)$$

the electric force is $\vec{F} = q\vec{\mathcal{E}} = -\nabla V$]. This problem may be olved exactly by completing squares in the total amiltonian

$$\begin{aligned}
\hat{H} &= \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2 - q\mathcal{E}\hat{x} \\
&= \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \left[\hat{x}^2 - \frac{2q\mathcal{E}}{m\omega^2}\hat{x}\right] \\
&= \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \left[\left(\hat{x} - \frac{q\mathcal{E}}{m\omega^2}\right)^2 - \left(\frac{q\mathcal{E}}{m\omega^2}\right)^2\right] \\
&= \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \left(\hat{x} - \frac{q\mathcal{E}}{m\omega^2}\right)^2 - \frac{(q\mathcal{E})^2}{2m\omega^2}
\end{aligned}$$

This is again the Hamiltonian of an harmonic oscillator, but with a translated position. Thus, the new eigenvalues are

$$E_n = E_n^0 - \frac{(q\mathcal{E})^2}{2m\omega^2} \qquad (16)$$

The electric field simply shifts all eigenvalues by a constant amount. The wavefunctions are all translated by an amount $(q\mathcal{E})/m\omega^2$. This is not really surprising: think about what happens in a vertical spring oscillating under the effect of gravity.

Now we can compare our results with perturbation theory assuming $q\mathcal{E}$ is small. What we need is:

$$\langle m^0|\hat{V}|n^0\rangle = -q\mathcal{E}\frac{x_0}{\sqrt{2}}\langle m^0|\hat{a}^\dagger + \hat{a}|n^0\rangle$$

$$= -q\mathcal{E}\frac{x_0}{\sqrt{2}}\left[\sqrt{n}\,\delta_{m,n-1} + \sqrt{n+1}\,\delta_{m,n+1}\right] \qquad (1$$

Thus we see that E_n^1 is zero:

$$\langle n^0|\hat{V}|n^0\rangle = 0 \qquad (18)$$

This is why it is important to have E_n up to order λ^2.
For the second order term we need

$$E_n^0 - E_m^0 = \hbar\omega(n-m)$$

$$|\langle m^0|\hat{V}|n^0\rangle|^2 = (q\mathcal{E})^2\frac{x_0^2}{2}\left[n\,\delta_{m,n-1} + (n+1)\,\delta_{m,n+1}\right] \qquad (1$$

Thus

$$E_n^2 = \frac{(q\mathcal{E})^2}{2\hbar\omega}\,\frac{\hbar}{m\omega}\sum_{m\neq n}\left[\frac{n\,\delta_{m,n-1} + (n+1)\,\delta_{m,n+1}}{n-m}\right]$$

$$= \frac{(q\mathcal{E})^2}{2m\omega^2}\left[\frac{n}{n-(n-1)} + \frac{(n+1)}{n-(n+1)}\right] = -\frac{(q\mathcal{E})^2}{2m\omega^2}$$

e energy is then

$$E_n = E_n^0 - \frac{(q\mathcal{E})^2}{2m\omega^2}$$

hich is exactly (16).

Let us also look at the eigenvectors in Eq (10):

$$|n\rangle = |n_0\rangle - \frac{(q\mathcal{E})}{\hbar\omega}\frac{x_0}{\sqrt{2}}\sum_{m\neq n}\frac{\left[\sqrt{n}\,\delta_{m,n-1} + \sqrt{n+1}\,\delta_{m,n+1}\right]|m_0\rangle}{n-m}$$

$$= |n_0\rangle - \frac{(q\mathcal{E})}{\hbar\omega}\frac{x_0}{\sqrt{2}}\left[\sqrt{n}\,|n_0-1\rangle - \sqrt{n+1}\,|n_0+1\rangle\right] \qquad (20)$$

his may look like a random state. But notice that

$$\hat{p}\,|n_0\rangle = \frac{i p_0}{\sqrt{2}}(\hat{a}^{\dagger} - \hat{a})\,|n_0\rangle = \frac{i p_0}{\sqrt{2}}\left[\sqrt{n+1}\,|n_0+1\rangle - \sqrt{n}\,|n_0-1\rangle\right]$$

o

$$\frac{1}{\sqrt{2}}\left[\sqrt{n}\,|n_0-1\rangle - \sqrt{n+1}\,|n_0+1\rangle\right] = i\frac{\hat{p}}{p_0}\,|n_0\rangle$$

us we may write (20) as

$$|n\rangle = |n_0\rangle - i\,\frac{(q\mathcal{E})}{\hbar\omega}\,\frac{x_0}{p_0}\,\hat{p}\,|n_0\rangle$$

The coefficient in front is

$$\frac{q\mathcal{E}}{\hbar\omega}\frac{x_0}{p_0} = \frac{q\mathcal{E}}{\hbar\omega}\frac{x_0^2}{\hbar} = \frac{q\mathcal{E}}{\hbar\omega}\frac{\hbar}{m\omega}\frac{1}{\hbar} = \frac{q\mathcal{E}}{m\omega^2}\frac{1}{\hbar}$$

Hence

$$\boxed{|m\rangle = \left[1 - i\left(\frac{q\mathcal{E}}{m\omega^2}\right)\frac{\hat{p}}{\hbar}\right]|m_0\rangle} \qquad (21)$$

Recall that the translation operator is $e^{-ia\hat{p}/\hbar}$. This new eigenvector therefore represents a spatial translation of the unperturbed eigenvector by an infinitesimal amoun $\frac{q\mathcal{E}}{m\omega^2}$. This is exactly what we found in the exact solut the only difference being that there the translation did not have to be infinitesimal.

The Helium atom

Consider the He atom, or any ion with 2 electrons, such as i^{+}, Be^{++}, etc. The Hamiltonian will contain the interaction of each electron with the nucleus, and their mutual repulsion:

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Z q^2}{r_1} - \frac{Z q^2}{r_2} + \frac{q^2}{r_{12}} \qquad (22)$$

where $q^2 = e^2/4\pi\varepsilon_0$ and $r_{12} = |\vec{r}_1 - \vec{r}_2|$. What I want to do is try and find the energy of the ground state supposing that the last term may be treated as a perturbation.

If the two electrons did not interact, the problem would be reduced to two independent hydrogen atoms. The ground state correspond to both in a singlet state

$$\frac{|+-\rangle - |-+\rangle}{\sqrt{2}}$$

hich allows for their spatial wavefunctions to be ymmetric, both corresponding to the ground state of the hydrogen atom

$$\Psi^0_{gs}(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) \qquad (23)$$

here

$$\psi_{100}(\vec{r}) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0} \qquad (24)$$

the unperturbed ground state energy is

$$E_{gs}^{0} = 2 Z^{2} E_{1} \qquad (25)$$

where $$E_{1} = -13.6 \text{ eV}$$

Now we want to find the correction to this energy if we assume that the last term in (22) is small. This correction is

$$E_{gs}^{1} = \langle gs | \frac{q^{2}}{r_{12}} | gs \rangle = \int \frac{q^{2}}{r_{12}} | \Psi_{gs}^{0} (\vec{r}_1, \vec{r}_2) |^{2} \, dV_1 \, dV_2 \qquad (26$$

This is not a simple integral to do because it involve 6 dimensions. But it can be done and the result is

$$E_{gs}^{1} = -\frac{5}{4} Z E_{1} \qquad (27)$$

Thus, the total energy of the ground state is

$$\boxed{E_{gs} = \left(2 Z^{2} - \frac{5}{4} Z \right) E_{1}} \qquad (28)$$

Below we compare this with experimental data (ionization energie

Ion	Z	$\lvert E_{exp}$ (eV)$\rvert$	$\lvert E_{gs}^{0}$ (eV)$\rvert$	$\lvert E_{gs}$ (eV)$\rvert$
He	2	78.62	108.24	74.42
Li^{+}	3	197.14	243.54	192.80
Be^{++}	4	369.96	432.96	365.31
B^{3+}	5	596.4	676.50	591.94
C^{4+}	6	876.2	974.16	872.69

VERY GOOD!!!

Bosons and Fermions in a potential well

The eigenfunctions and eigenenergies of the infinite potential well are

$$\psi_n(x) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi x}{a}\right) \qquad 0<x<a \qquad (29)$$

$$E_n = \frac{\hbar^2\pi^2 n^2}{2ma^2}, \quad n=1,2,3,\ldots \qquad (30)$$

where a is the length of the well.

Suppose we now have two non-interacting particles n the well. If the particles are identical, they will have to live in completely symmetric or completely anti-symmetric spaces.

The ground state is $n_1=1$, $n_2=1$, and it is symmetric

$$\psi_{11}(x_1,x_2) = \psi_1(x_1)\,\psi_1(x_2) \qquad (31)$$

he first excited state is $n_1=1$, $n_2=2$ or vice-versa. If he particles were distinguishable, this energy would be doubly degenerate. But the symmetrization requirement makes this state unique. For symmetric systems we must ave

$$\psi_{12}^{S}(x_1,x_2) = \frac{\psi_1(x_1)\,\psi_2(x_2) + \psi_2(x_1)\,\psi_1(x_2)}{\sqrt{2}} \qquad (32)$$

whereas in the anti-symmetric configuration

$$\psi_{12}^{A}(x_1,x_2) = \frac{\psi_1(x_1)\,\psi_2(x_2) - \psi_2(x_1)\,\psi_1(x_2)}{\sqrt{2}} \qquad (33)$$

Two Bosons or Fermions may sometimes repel each other if they ever get too close. For instance, if two atoms get very close to one another, the electron clouds will overlap, leading to a strong repulsion. This may be modelled by a potential

$$\hat{V} = a V_0 \, \delta(x_1 - x_2) \qquad (34)$$

It is zero if they are sepparated, but becomes infinite if they get too close together. This is what is called a <u>hard</u> <u>sphere</u> <u>approximation</u>.

Let us treat this term using perturbation theory.

<u>Ground State</u>

$$E^1_{gs} = \langle 11 | \hat{V} | 11 \rangle = a V_0 \int \delta(x_1 - x_2) \, \psi_1^2(x_1) \, \psi_2^2(x_2) \, dx_1 dx_2$$

$$= a V_0 \left(\frac{2}{a}\right)^2 \int_0^a \sin^4\left(\frac{\pi x_1}{a}\right) dx_1$$

$$= a V_0 \frac{4}{a^2} \left(\frac{3a}{8}\right)$$

$$E^1_{gs} = \frac{3}{2} V_0$$

Thus, to first order

$$E_{gs} = 2\left(\frac{\pi^2 \hbar^2}{2ma^2}\right) + \frac{3}{2} V_0 \qquad (35$$

Similarly, for the first excited state :

$$E_{es}^{1} = \langle 1 2 | \hat{V} | 1 2 \rangle = aV_0 \int \delta(x_1 - x_2)\, |\Psi_{12}(x_1, x_2)|^2 dx_1\, dx_2$$

$$= aV_0 \int |\Psi_{12}(x_1, x_1)|^2 dx_1$$

ut

$$\Psi_{12}^{A}(x_1, x_1) = 0$$

$$\Psi_{12}^{S}(x_1, x_1) = \sqrt{2}\, \psi_1(x_1)\, \psi_1(x_1)$$

Thus, the contribution to an anti-symmetric state is zero, whereas for a symmetric state we have

$$E_{es}^{1} = a\, V_0\; 2 \left(\frac{2}{a}\right)^2 \int_0^a \sin^2\!\left(\frac{\pi x_1}{a}\right) \sin^2\!\left(\frac{2\pi x_1}{a}\right) dx_1$$

$$= a V_0\, 2 \frac{4}{a^2}\, \frac{a}{4} = 2V_0$$

Thus, the energy of the first excited state is, for the ymmetric state,

$$E_{es} = \frac{\pi^2 \hbar^2}{2ma^2} + \frac{4\pi^2 \hbar^2}{2ma^2} + 2V_0 \qquad (36)$$